

PTO 04-3957

Japanese Patent
Document No. H11-79702

METHOD FOR MODIFYING METHANOL

[Metanoru no Kaishitsu Hoho]

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UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D.C.

June 2004

Translated by: Schreiber Translations, Inc.

Country : Japan

Document No. : H11-79702

Document Type : Kokai

Language : Japanese

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IPC : C 01 B 3/38
B 01 J 23/80
38/12
H 01 M 8/06

Application Date : September 3, 1997

Publication Date : March 23, 1999

Foreign Language Title : Metanoru no Kaishitsu Hoho

English Title : METHOD FOR MODIFYING METHANOL

(54) Title of the invention

METHOD FOR MODIFYING METHANOL

(57) Summary

Objective: To provide a method for modifying methanol capable of modifying methanol in a high efficiency over an extended period by perpetuating a high activity state of a modifying catalyst.

Solution mechanism: In a method for manufacturing a modified gas inclusive of gaseous hydrogen and gaseous carbon dioxide by executing an operation for reacting & modifying methanol in the presence of a modifying catalyst, a regenerating operation for regenerating the aforementioned modifying catalyst by feeding air into the aforementioned modifying catalyst is carried out upon the achievement of a certain designated degree of degradation by said catalyst, followed by the resumption of the aforementioned modifying operation, and a modified gas is manufactured by repeating said modifying reaction operations and regenerating operations.

¹ Numbers in the margin indicate pagination in the foreign text.

Claim 1

A method for modifying methanol characterized,

With regard to a method for manufacturing a modified gas inclusive of gaseous hydrogen and gaseous carbon dioxide by executing an operation for reacting & modifying methanol in the presence of a modifying catalyst,

By the facts

That a regenerating operation for regenerating the aforementioned modifying catalyst by feeding air into the same is carried out upon the achievement of a certain designated degree of degradation by the aforementioned modifying catalyst,

That the aforementioned modifying reaction operation is subsequently resumed, and

That a modified gas is manufactured by repeating such modifying reaction operations and regenerating operations.

Detailed explanation of the invention

[0001]

(Technical fields)

The present invention concerns a method for modifying methanol orchestrated in the context of manufacturing a hydrogen-containing gas used for hydrogen fuel batteries, for hydrogenating various organic compounds, and/or for various industrial water

supplies, and in particular, a method for activating and regenerating a modifying catalyst used for said method.

[0002]

(Prior art)

Various research & development efforts have in recent years been channeled into the applications of methods for modifying methanol to hydrogen fuel batteries designed to be mounted on automobiles, in particular. The method for modifying methanol signifies a method for manufacturing a modified gas inclusive of gaseous hydrogen and gaseous carbon dioxide by executing a modifying reaction operation wherein methanol and water are reacted in the vapor phase in the presence of a modifying catalyst.

[0003]

An oxide mixture constituted by copper oxide (CuO), zinc oxide (ZnO), and alumina (Al_2O_3), furthermore, is being used as the aforementioned modifying catalyst. Moreover, the aforementioned modifying reaction operation is normally carried out at $200 \sim 300^\circ\text{C}$. As far as the aforementioned modifying method of the prior art is concerned, furthermore, the activity of the modifying catalyst is generally high in the initial phase of the aforementioned modifying reaction operation, due to which the reaction is induced at a relatively low temperature initially, and the reaction temperature is elevated in accordance with an activity loss.

[0004]

(Problems to be solved by the invention)

In a case where such a temperature elevation schedule is orchestrated, however, the pulverization of the modifying catalyst is likely to occur in accordance with the temperature gain, and since the catalyst layer becomes congested, the pressure loss within the catalyst layer increases. The production efficiency deteriorates as a result of such a pressure loss. A considerable thermal energy, furthermore, is required in the course of the aforementioned temperature elevating operation.

[0005]

Modifying catalysts have therefore been exchanged at appropriate stages in the prior art in consideration of the production efficiency, overall thermal efficiency, and the concomitant cost appreciation. In order to thus exchange modifying catalysts, however, an extended time becomes required for retrieving an old modifying catalyst from a reaction tank, for cleaning, and for filling a new modifying catalyst into said reaction tank. In the meantime, absolutely no modifying reaction operation can be carried out, and the modified gas cannot be manufactured. Such circumstances greatly hinder the operation of an automobile in a case where a methanol modifying device is mounted on said automobile and where the gaseous hydrogen obtained from this device is used for a hydrogen fuel battery.

[0006]

As a method for solving such a problem, Japanese Patent Application Publication Kokai No. Sho 62[1987]-36001 Gazette proposes a method wherein the activity of a catalyst is recovered by mandating intermittent co-existences of the fuel gas, modified gas, and oxygen within itself over a 20-hour period. Even if the co-existence of oxygen during the modifying reaction is mandated in this case, however, it is impossible to stop the degradation. This fact will be discussed in Application Example 4 on a later occasion.

[0007]

Japanese Patent Application Publication Kokai No. Hei 4[1992]-200640 Gazette, furthermore, proposes the subjecting of a modifying catalyst to an atmosphere characterized by a molecular oxygen concentration of 5 mol% or lower within a temperature range of 120°C ~ 650°C. Japanese Patent Application Publication Kokai No. Hei 9[1997]-75734 Gazette, furthermore, proposes a scheme for subjecting a modifying catalyst to (1): A preliminary treatment by a hydrogen-containing gas, (2): An oxidation treatment by an oxygen-containing gas, and then (3): A regenerating treatment by a reducing gas. In the context of orchestrating both of the aforementioned schedules, however, it is necessary to provide a special gas feeding device wherein the oxygen concentration and/or hydrogen concentration are regulated.

[0008]

In each of the application examples of the methods disclosed in the aforementioned three Gazettes, furthermore, the duration of the regenerating treatment is 10 min. at the minimum, and 10 ~ 30 hours in most cases. The degree of degradation, furthermore, is simply measured by means of gas chromatography, etc. in these methods, and no mechanism for detecting the degree of degradation is provided. Thus, the aforementioned methods, which may mandate a special gas feeding device and/or extended regenerating treatment time and/or may possess no simple mechanism for detecting the degree of degradation, are, due to their inability to perpetuate high degrees of modification, difficult to orchestrate not only for mobile purposes (e.g., automotive, etc.) but also for immobile purposes.

[0009]

The present invention attempts, in acknowledgment of these problems of the prior art, to provide a method for modifying methanol capable of modifying methanol in a high efficiency over an extended period by perpetuating a high activity state of a modifying catalyst.

[0010]

(Mechanism for solving the problems)

The present invention concerns a method for modifying methanol characterized, with regard to a method for manufacturing a modified gas inclusive of gaseous hydrogen and gaseous carbon

dioxide by executing an operation for reacting & modifying methanol in the presence of a modifying catalyst, by the facts that a regenerating operation for regenerating the aforementioned modifying catalyst by feeding air into the same is carried out upon the achievement of a certain designated degree of degradation by the aforementioned modifying catalyst, that the aforementioned modifying reaction operation is subsequently resumed, and that a modified gas is manufactured by repeating such modifying reaction operations and regenerating operations.

[0011]

The most notable aspects of the present invention lie in the facts that, in a case where a modifying catalyst has become degraded down to a certain degree of activity, an attempt is made to activate & regenerate said modifying catalyst by feeding air into it, that the modifying reaction is then resumed, and that these cycles are repeated.

[0012]

Next, the functions and effects of the present invention will be explained. As will be discussed later in detail, as far as the present invention is concerned, in a case where a modifying catalyst has become degraded in the course of the aforementioned modifying reaction operation and where its activity has dropped to or below a certain designated degree of degradation, the modifying reaction operation is temporarily halted, and the modifying catalyst is then subjected to a regenerating operation for feeding air into it. As a result, the modifying catalyst becomes

regenerated at an activity virtually equal to its initial activity.

[0013]

The modifying reaction operation is then resumed. Upon the achievement, once again, of the aforementioned degree of degradation during this modifying reaction operation, a regenerating operation similar to the aforementioned one is carried out. For these reasons, the high activity state of the modifying catalyst is perpetually maintained, and methanol can be modified in a high efficiency over an extended period. /3

[0014]

In a case where a certain designated degree of degradation of the aforementioned modifying catalyst becomes achieved with regard to a method for manufacturing a modified gas inclusive of gaseous hydrogen and gaseous carbon dioxide or gaseous hydrogen, gaseous carbon, and gaseous nitrogen, furthermore, it becomes possible to realize a method for manufacturing a modified gas by modifying methanol by feeding air into the aforementioned modifying catalyst as an attempt to regenerate it, by executing the aforementioned modifying reaction operation after this regenerating operation, and by repeating such modifying reaction operations and regenerating operations. In this case, too, effects similar to the aforementioned ones can be achieved.

[0015]

Next, favorable embodiments for executing the aforementioned modifying method will be explained. First, it is desirable to

orchestrate a mechanism for detecting the degree of degradation for the purpose of detecting the aforementioned designated degree of degradation. It becomes possible to automatically detect the designated degree of degradation in such a case.

[0016]

Next, a mechanism for detecting at least one type selected from among the temperature, CO concentration, methanol concentration, hydrogen concentration, CO₂ concentration, H₂O concentration, and gas flow rates is desirable as the aforementioned mechanism for detecting the degree of degradation. It is especially desirable, furthermore, for the mechanism for detecting the degree of degradation to possess not only a mechanism for detecting at least one type selected from among the temperature, CO concentration, methanol concentration, hydrogen concentration, CO₂ concentration, H₂O concentration, and gas flow rates but also a mechanism for determining the degree of degradation based on the activity ratio of the modifying catalyst between the inlet and outlet sides.

[0017]

It is especially desirable, furthermore, for the mechanism for detecting the degree of degradation to possess not only a mechanism for detecting at least one type selected from among the temperature, CO concentration, methanol concentration, hydrogen concentration, CO₂ concentration, H₂O concentration, and gas flow rates but also a mechanism for determining the timing of an oncoming regenerating operation by defining the detected value as

the degree of degradation, by calculating the ratio between this degree of degradation and the designated degree of degradation, and by correlationally predicting the time elapsed till the achievement of the designated degree of degradation.

[0018]

It is especially desirable, furthermore, for the mechanism for detecting the degree of degradation to possess not only a mechanism for detecting at least one type selected from among the temperature, CO concentration, methanol concentration, hydrogen concentration, CO₂ concentration, H₂O concentration, and gas flow rates but also a mechanism for determining the timing of an oncoming regenerating operation by comparing the ratio of the respective activities of the modifying catalyst on the inlet and outlet sides with the designated value and by correlationally predicting the time elapsed till the achievement of the designated degree of degradation.

[0019]

Next, it is desirable for the aforementioned modifying catalyst to be provided by supporting, on a metallic or cordierite ceramic carrier, a modifying catalyst component constituted mainly by the oxide of any one of copper, zinc, aluminum, and chromium or a corresponding oxide mixture of two or more types.

[0020]

It is especially desirable, furthermore, to schedule a format whereby a modifying catalyst is provided by supporting, on a metallic or cordierite ceramic carrier, a modifying catalyst

component constituted mainly by the oxide of any one of copper, zinc, aluminum, and chromium or a corresponding oxide mixture of two or more types and whereby a mechanism for detecting the degree of degradation designed to determine the timing of an oncoming regenerating operation by measuring the respective temperatures of the modifying catalyst on the inlet and outlet sides as well as the outlet CO concentration, by comparing the designated values of the outlet CO concentration specific respectively to the temperatures of the inlet and outlet sides, and by correlationally predicting the time elapsed till the achievement of the designated degree of degradation. In this embodiment, an effect of maintaining the outlet CO concentration at a constant level can be achieved even in a case where the catalyst has become impossible to regenerate due to its sintering.

[0021]

Next, the catalyst component of the aforementioned modifying catalyst of the present invention may, for example, be instantiated by mixed oxides of CuO , ZnO , & Al_2O_3 , their copper-, chromium-, and/or zinc-supported counterparts, and their oxides. An unsupported catalyst wherein a catalyst component alone is formed into the shape of a pellet or tablet is also conceivable. The aforementioned modifying catalyst may also be instantiated by a supported catalyst whereby a catalyst component (e.g., the aforementioned oxide mixture, etc.) is supported on a metallic carrier obtained by configuring a metal (e.g., stainless steel,

etc.) in a steric shape (e.g., honeycomb, etc.) (refer to Figure 4).

[0022]

Either of the aforementioned unsupported catalyst and supported catalyst may be used in the present invention. Incidentally, the latter type, namely the supported catalyst, ensures an excellent initializability due to its thermal capacity. Since the contact area between the reaction gas (gaseous mixture of methanol + water) and the modifying catalyst can be enlarged, furthermore, an excellent production efficiency can be achieved, and a light weight of the catalyst layer per unit volume suffices. In this case, furthermore, the liquid spatial velocity of the modifying reaction operation based on the methanol standard is as high as 2 ~ 7/hr, for example, and the productivity is thus high. Incidentally, the aforementioned spatial velocity is as low as approximately 0.3 ~ 1.0/hr in the case of the former, namely unsupported, catalyst.

[0023]

The aforementioned "designated degree of degradation" signifies the degree of activity of the catalyst at which the aforementioned regenerating operation becomes necessary due to the loss of the catalyst activity in the course of an extended modifying reaction operation. Said designated degree of degradation may, for example, be orchestrated to coincide with the point in time at which the temperature of the catalyst layer has risen to a certain designated temperature within a range of 180 ~

320°C. Most importantly, the modifying reaction operation is normally carried out within a temperature range of 180 ~ 320°C, and a temperature 0.1 ~ 140°C higher than the temperature of the modifying reaction operation is orchestrated to coincide with the designated degree of degradation.

[0024]

The aforementioned designated degree of degradation may also be determined by measuring the outlet CO concentration. In this case, the point in time at which the CO concentration has reached a certain level within a CO concentration range of 0.01 ~ 2% may, for example, be orchestrated to coincide with the designated degree of degradation. In a case where the method of the present invention for modifying methanol is utilized as a hydrogen source for a low-temperature fuel battery (solid polymer electrolyte-type fuel battery or phosphoric acid-type fuel battery), for example, CO serves as a poisonous substance for the electrode catalyst of the fuel battery, and therefore, it is necessary to inhibit its concentration at the lowest level possible.

[0025]

An aqueous gas shift reaction or a method for selectively oxidizing or methanizing CO is conceivable as a method for lowering the CO concentration of the modified gas by means of an aftertreatment performed after the modifying method of the present invention. In any event, however, it is necessary to lower the CO concentration as much as possible at the time of modification for purposes of providing a compact reaction apparatus and for

sufficiently lowering the concentration of CO fed into the fuel battery. Such a selection of the CO concentration as a parameter of the designated degree of degradation is suitable in a case where the present invention is applied to a fuel battery system, etc. /4

[0026]

The aforementioned designated degree of degradation may, for example, be determined by measuring the degree of modification during the modifying reaction operation, namely the ratio (%) of methanol modified into gaseous hydrogen. In this case, the point in time at which the degree of modification has reached a certain level within a degree of modification range of 80 ~ 99.9% may, for example, be orchestrated to coincide with the designated degree of degradation.

[0027]

The aforementioned degree of modification may also be detected by measuring, at the catalyst outlet, at least one type selected from among the hydrogen concentration, CO₂ concentration, methanol concentration, H₂O concentration, and gas flow rates. In other words, the degree of modification can be calculated, in a simplified manner, from the relationships of the respective quantitative ratios of methanol and water, which are known in advance, not only with one, two, or more parameters selected from among the hydrogen concentration, CO₂ concentration, methanol concentration, H₂O concentration, and gas flow rates, which have

been preliminarily measured, but also with the degree of modification.

[0028]

The designated degree of degradation parameterized either by the temperature or CO concentration in the course of the modifying reaction operation or by the simplified degree of modification can be discerned by detecting any one parameter selected from among the temperature, concentrations of various matters, and gas flow rates, and accordingly, an excellent responsiveness can be achieved. In a case where the degree of modification is calculated by measuring all the gaseous components, on the other hand, the designated degree of degradation can virtually be gauged in terms of the degree of modification.

[0029]

Next, it is desirable for the air to be fed in the course of the aforementioned regenerating operation in such a way that the gas spatial velocity within the catalyst layer will be confined to a range of 200 ~ 800/hr. Incidentally, this spatial velocity represents the value of a case where the air temperature is designated at 25°C. In a case where this value is lower than 200/hr, an extended regenerating operation becomes required, whereas in a case where the same exceeds 800/hr, the surface temperature of the modifying catalyst becomes elevated to an excessively high level, as will be shown on a later occasion, and its activity may deteriorate due to the sintering ([reiterated]) of the modifying catalyst surface. The air was fed within this

range in the application examples discussed later, although the volume of air may be enlarged for accelerating the reaction so long as the temperature does not exceed 320°C.

[0030]

In other words, the temperature of the modifying catalyst becomes elevated as a result of the feeding of air during the aforementioned regenerating operation. In this case, the temperature presumably becomes elevated by the reaction heat generated in the course of the reaction of the catalyst component(s) which has temporarily been reduced into Cu, etc. by the gaseous hydrogen of the modified gas during the modifying reaction operation with the oxygen content of the aforementioned air, which entails the regeneration of the oxide(s).

[0031]

In this context, the temperature gain of said modifying catalyst is detected, and the feeding of the air, namely the regenerating operation, is terminated at a stage where the temperature of the catalyst layer has reached a certain value during the regenerating operation. It is desirable for the upper limit on the aforementioned temperature to be 450°C, preferably 320°C. In a case where the temperature is higher than this threshold, the catalyst performances may deteriorate due to the sintering of the surface of the modifying catalyst.

[0032]

It is desirable for the action for feeding air in the course of the aforementioned regenerating operation to be invoked

immediately after the modifying reaction operation has been terminated. In such a case, the regenerating operation can be initialized at a high temperature (180 ~ 320°C), and accordingly, an efficient regenerating operation can be carried out. It is also possible to execute the regenerating operation by feeding air after the reaction gas and modified gas within the catalyst layer have been purged by feeding gaseous nitrogen (N₂) upon the termination of the modifying reaction operation. In this case, an effect of moderating the generation of heat attributed to the oxidation of the residual modified gas or methanol within the catalyst layer can be achieved. For the purpose of executing an efficient regenerating operation, furthermore, it is desirable for the temperature of the catalyst layer at the beginning of the air feeding operation to be designated within a range of 100 ~ 450°C, preferably 180 ~ 300°C.

[0033]

The regenerating operation of a case where the designated degree of degradation of the modifying catalyst has reached a certain level has been discussed above, whereas in a case where the gas obtained in the present invention as a result of the modification of methanol is applied to a modifying apparatus to be mounted on an automobile, the aforementioned regenerating operation can be executed within a brief period upon the completion of the operation of the automobile (e.g., at night, etc.). In such a case, a modifying reaction operation can be executed on the following morning by using a modifying catalyst

characterized invariably by a high activity state. A regenerating operation can, furthermore, be executed during a brief stoppage of the system (e.g., refueling operation, etc.), and at the time of initializing the next cycle, a modifying reaction operation can be executed by using a modifying catalyst characterized by a high activity state.

[0034]

(Application embodiments of the invention)

Application Embodiment 1

The methanol modification method of an application embodiment of the present invention will be explained with reference to Figures 1 ~ 3. The methanol modification method of the present application embodiment is, as Figures 2 & 3 indicate, a method for manufacturing a modified gas comprised of gaseous hydrogen and gaseous carbon dioxide by means of a modifying reaction operation whereby methanol and water are mutually reacted in the vapor phase in the presence of the modifying catalyst (11).

[0035]

In a case where the designated degree of degradation (e.g., designated temperature) of the aforementioned modifying catalyst (11) has reached a certain level in the course of the aforementioned modifying reaction operation (Figure 2), furthermore, a regenerating operation is executed by feeding air into the aforementioned modifying catalyst (11) in order to

regenerate the same, followed by the resumption of the aforementioned modifying reaction operation, and a modified gas is manufactured by repeating such modifying reaction operations and regenerating operations.

[0036]

In the following, the aforementioned modifying method will be explained in detail. First, Figure 3 is an approximate demonstrational diagram pertaining to a methanol modification apparatus to be used for the aforementioned modifying method. The present apparatus possesses the reaction tank (1), which is filled with the modifying catalyst (11), the solution tank (21), which is connected to said reaction tank (1) via the pump (22), the vaporizer (23), & the feed material pipe (24), and the blower (31), which is connected to the aforementioned reaction tank (1) via the air pipe (32). The modified gas pipe (12) for transporting the modified gas and the purge pipe (16), furthermore, are configured on the lower stream side of the reaction tank (1). The outer wall of the reaction tank (1) is heated by a heater for feeding heat into the modifying catalyst (11).

[0037]

Also configured, furthermore, is the controller (3), which controls the operation of the aforementioned pump (22) or blower (31) by detecting the temperature, various concentrations (e.g., CO concentration, etc.), or gas flow rates within the aforementioned reaction tank (1). Said controller, furthermore,

possesses the catalyst layer inlet side temperature sensor (35), which is configured within the reaction tank (1), and/or the catalyst layer outlet side temperature sensor (36), and/or the inlet side concentration sensor or gas flow rate sensor (37), and/or the outlet side concentration sensor or gas flow rate sensor (38).

[0038]

A case where the aforementioned modifying method is executed by using the aforementioned modification apparatus will be demonstrated. First, the liquid mixture (20) of 5 methanol and water within the solution tank (21) is fed, via the pump (22), into the reaction tank (1), more specifically into the modifying catalyst (11) within the reaction tank (1). At this stage, the aforementioned liquid mixture is vaporized by the vaporizer (23), which is being heated at approximately 300°C, and then transported, via the feed material pipe (24), in a gaseous state. The outer wall of the reaction tank (1) is heated at approximately 290°C. A modifying reaction operation is then executed at an average catalyst layer temperature of approximately 280°C, and a modified gas comprised of gaseous hydrogen (H₂) and gaseous carbon dioxide (CO₂) becomes transported via the modified gas pipe (12).

[0039]

While the modifying reaction operation is thus being carried out, the modifying catalyst (11) becomes gradually degraded. Upon the detection, by the temperature sensors (35) & (36), of the fact

that the temperature of the modifying catalyst (11) within the reaction tank (1) (e.g., average temperature of the inlet- & outlet-side temperatures) has become elevated to the level corresponding to the specifiably designated degree of degradation (e.g., 285°C), furthermore, the controller (3) stops the pump (22). At the same time, the heating of the reaction tank (1) by the heater is stopped for terminating the feeding of the aforementioned liquid mixture (20). As a result, the modifying reaction operation becomes halted. Next, the controller (3) activates the blower (31) and feeds air, via the air pipe (32), into the reaction tank (1) for executing a regenerating operation. The gas prevailing at the time of the regenerating operation is discharged via the purge pipe (16).

[0040]

The temperature variations within the reaction tank (1) during the aforementioned modifying reaction operation and regenerating operation and the variation of the degree of modification during the modifying reaction operation are outlined in Figure 1, whereas Figure 2 is a partially magnified demonstrational diagram corresponding to the same. As both figures indicate, the degree of modification gradually decreases over time, as a result of which the heat absorption capacity of the modifying reaction diminishes, accompanied by a gradual temperature gain of the catalyst layer within the reaction tank. In a case where the catalyst layer temperature has become elevated to the level designated to coincide with the designated degree of

degradation (285°C in the aforementioned embodiment), furthermore, the aforementioned regenerating operation is carried out. Subsequently, the modifying reaction operation is carried out once again. As a result, the degree of modification comes to drop, rise, and drop in a zigzag fashion, as the curves (41) ~ (45) in Figure 1 indicate. The temperature of the catalyst layer, too, varies in a zigzag fashion, as the curves (410) ~ (450) indicate.

[0041]

Figure 2, furthermore, shows the temperature state of the catalyst layer during the regenerating operation. As the same figure indicates, the temperature rises gradually in the course of the modifying reaction operation, and upon the achievement of the designated temperature parameterized as the designated degree of degradation, the feeding of the liquid mixture (20) is stopped, as has been mentioned earlier, whereas the heating action of the heater of the reaction tank (1) is terminated, and after the temperature has been lowered to the regeneration initialization temperature, air is fed. For these reasons, the temperature of the catalyst layer becomes elevated as a result of an oxidizing reaction, as has been mentioned earlier. As far as the present example is concerned, therefore, the regenerating operation is carried out in a state where the temperature of the catalyst layer is being maintained at or below the upper limit of 320°C. After the regenerating operation has been completed, furthermore, the modifying reaction operation is executed once again. The

modifying reaction operations and regenerating operations are repeated according to the aforementioned schedule.

[0042]

Incidentally, the state where the degree of modification has become lowered due to a failure to execute the aforementioned regenerating operation is indicated by the dotted curve (49) in Figure 1. The modifying catalyst orchestrated for the aforementioned example, furthermore, is a modifying catalyst obtained by supporting, on a honeycomb-shaped metal carrier, a catalyst component comprised of $\text{CuO-ZnO-Al}_2\text{O}_3$ (refer to Figure 4 pertaining to Application Embodiment 2).

[0043]

As can be discerned from the aforementioned descriptions, the modifying method of the present invention is capable of modifying methanol in a high efficiency over an extended period by perpetuating a high activity state of a modifying catalyst.

[0044]

Application Embodiment 2

A concrete embodiment for manufacturing a modified gas by using the modification apparatus shown in Application Embodiment 1 will be explained in the present example. First, one obtained by supporting the catalyst component (10) on the metal carrier (5) is used as the modifying catalyst (11), as Figure 4 indicates. The metal carrier (5) is provided by configuring wavy sheets (52) between large numbers of flat sheets (51) and by then joining

both, resulting in the manifestation of a 600 cells/inch² honeycomb structure.

[0045]

The catalyst component (10) abides in a state where it is being adhered to the surfaces of the aforementioned flat sheets (51) & wavy sheets (52). Stainless steel sheets are each used as the flat sheets (51) & wavy sheets (52) of the aforementioned metal carrier (5). The supported quantitative ratio of the catalyst component (10) with respect to the metal carrier is 172 g/L. The catalyst component is constituted by approximately 42 wt% CuO-approximately 47 wt% ZnO-approximately 11 wt% Al₂O₃. At the beginning of a modifying reaction operation, a reducing treatment was performed at an average catalyst layer temperature of 200°C and at a gas spatial velocity of 2,000/hr over a 4-hour period. A modifying reaction operation was then carried out.

[0046]

In the course of the modifying reaction operation, a liquid mixture comprised of 47 wt% of methanol and 53 wt% of water was vaporized within a vaporizer and then fed into the catalyst layer within a temperature range of 260 ~ 290°C at a methanol spatial velocity (LHSV-M) = 2 h⁻¹. The composition of the modified gas obtained as a result of the modifying reaction operation was gas chromatographically analyzed. In the course of the aforementioned modifying reaction operation, furthermore, the degree of degradation was designated to coincide with a catalyst layer inlet-side temperature of 270°C.

[0047]

At a point in time where catalyst layer inlet-side temperature had become elevated to 270°C, namely the aforementioned designated degree of degradation, the modifying reaction operation was halted, and a regenerating operation was carried out immediately thereafter. The regenerating operation was carried out over a 10-min. period by feeding air at approximately 25°C into the catalyst layer at a rate of 0.2 ~ 0.4 L/min., namely at a spatial velocity of 400 ~ 800/hr. The air feeding ratio, furthermore, was adjusted during the aforementioned regenerating operation for preventing the temperature of the catalyst layer from exceeding 320°C. Incidentally, the time required for regeneration was within 5 min. since the temperature variation. After the aforementioned regenerating operation had been completed, a modifying reaction operation was carried out, once again, according to procedures identical to the aforementioned ones, followed by the repetitions of similar regenerating operations & modifying reaction operations.

[0048]

Figure 5 shows the catalyst layer temperature and degree of modification during the period of 380th ~ 410th hour marks since the beginning of the use of the catalyst layer in a case where the aforementioned modifying reaction operations and regenerating operations were repeated. The duration of the regenerating operation, furthermore, is indicated by an arrow in the upper portion of the same figure. The CO concentration within the

modified gas at the beginning of each air feeding cycle and the concomitant catalyst layer inlet-side temperature, furthermore, are shown in Table I.

[0049]

[Table 1]

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Table I

Regeneration time (hrs)	CO concentration (%)		Inlet-side temperature (°C)	
	Before regenerati on	After regenerati on	Before regenerati on	After regeneratio n
385	0.494	0.477	270	269
393	0.499	0.501	271	270
401	0.535	0.513	270	270

[0050]

It can be discerned from the same figure and Table I that the temperature of the catalyst layer is perpetuated within a range of approximately 250 ~ 310°C in the course of the modifying reaction operation and that the degree of modification is concomitantly

maintained within a range of 95 ~ 100%. It can also be seen that the degree of modification becomes improved after each regenerating operation.

[0051]

Application Embodiment 3

The present example pertains to an embodiment wherein a regenerating operation is initially carried out by purging the catalyst layer with 1 L/min. of gaseous nitrogen (N_2) over a 10-min. period, wherein air is then fed into the catalyst layer at a rate of 0.2 ~ 0.4 L/min., and wherein a modifying reaction operation is carried out once again approximately 12 hours later.

[0052]

The duration of the aforementioned regenerating operation, furthermore, is indicated by an arrow in the upper portion of the same figure. In this case, an outlet CO concentration of 0.53% is designated as the designated degree of degradation. In a case where the outlet CO concentration had exceeded 0.53%, the aforementioned regenerating operation was carried out. The CO concentration within the modified gas at the beginning of each air feeding cycle and the concomitant catalyst layer inlet-side temperature, furthermore, are shown in Table II.

[0053]

[Table 2]

Table II

Regeneration time (hrs)	CO concentration (%)		Inlet-side temperature (°C)	
	Before regenerati on	After regenerati on	Before regenerati on	After regeneratio n
531	0.538	0.522	274	275
540	0.533	0.520	274	274
549	0.532	0.511	274	275

[0054]

It can be discerned from the same figure and Table II that a high degree of modification can be perpetuated over an extended period even in a case where a regenerating operation is carried out after a gaseous N₂ purging treatment and where a modifying reaction operation is carried out approximately 12 hours after said regenerating operation. It can also be seen that the degree of modification is improved after each regenerating operation.

[0055]

Incidentally, a gaseous mixture of N_2 and CO_2 or H_2O may be used in place of the aforementioned gaseous N_2 , and a mobile modification apparatus can easily be operated by removing the oxygen content of air by means of oxidation with hydrogen and/or CO within the feed methanol or modified gas.

Application Embodiment 4

As far as the present example is concerned, a modifying reaction is, as Table III indicates, induced in the first place in the presence of a catalyst identical to that used in Application Embodiment 2 under identical conditions, whereas a fuel gas alone was fed, according to the procedures prescribed in Japanese Patent Application Publication Kokai No. Sho 62[1988]-36001, into a catalyst the degree of modification of which had deteriorated to 87% (1 in the table), whereas air was introduced into the catalyst during the modifying reaction. After the co-existence of the fuel gas, modified gas, and oxygen (air) within the catalyst had been mandated for 30 ~ 50 min., a modifying reaction was induced under the co-pervasion of said the fuel gas, modified gas, and oxygen (air). The degree of modification and temperature of this case are shown in the same table (2 & 4 in the table). The degree of modification and temperature of a case where the feeding of air had then been stopped and where the fuel gas alone had been fed are also shown (3 & 5 in the table).

[0057]

As Table III clearly indicates, even if the co-existence of the fuel gas, modified gas, and oxygen (air) within the catalyst is mandated, no regeneration occurs, and the degree of modification cannot be recovered. The degree of modification and temperature of a case where the regenerating operation of the present invention was subsequently carried out are shown in the same table. The activity of the modifying catalyst becomes recovered as a result of the regenerating operation of the present invention, accompanied by the invigoration of an endothermic reaction and a catalyst layer inlet temperature loss, and the degree of modification becomes recovered to 99% or higher, which is virtually identical to the initial value at the beginning of modification (6 & 7 in the table).

[0058]

[Table 3]

Table III: Modification performances under the co-pervasion

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of oxygen as well as in the presence/absence of regeneration

	(A)	LHSV-M (h ⁻¹)	Gas temperature (°C)		Catalyst layer temperature (°C)		(B)	(C)	(D)
			Inlet	Outlet	Inlet	Outlet			
1	(E)	2.0	299	265	294	272	292	0.3 9	87
2	(F)	2.0	301	263	325	268	291	0.3 3	86
3	(E)	2.0	299	267	294	273	291	0.3 8	86
4	(G)	2.0	241	257	369	260	293	0.3 5	88
5	(E)	2.0	298	265	297	271	290	0.4 0	85
6	(G)	2.0	228	266	314	273	290	0.5 3	99.8
7	(E)	2.0	300	261	268	272	289	0.4 7	99.2

[(A): Fed matters; (B): Reaction tank wall temperature (°C); (C): Outlet CO, dry, vol%; (D): Degree of modification (%); (E): Methanol & water; (F): Methanol & water (air: 0.15 L/min.); (G): Methanol & water (air: 0.28 L/min.)]

[0059]

(Effects of the invention)

The present invention provides a method for modifying methanol capable of modifying methanol in a high efficiency over an extended period by perpetuating a high activity state of a modifying catalyst.

Brief explanation of the figures

Figure 1: A diagram which shows the relationships among the duration of a modifying reaction operation, degree of modification, and catalyst layer temperature in Application Embodiment 1.

Figure 2: A diagram which shows the temperature variation before/after the regenerating operation in Application Embodiment 1.

Figure 3: A demonstrational diagram pertaining to the modification apparatus of Application Embodiment 1.

Figure 4: A demonstrational diagram pertaining to the metal-supported catalyst of Application Embodiment 2.

Figure 5: A diagram which shows the relationships among the duration of a modifying reaction operation, degree of modification, catalyst layer temperature, etc. in Application Embodiment 2.

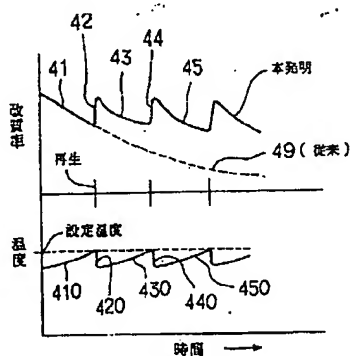
Figure 6: A diagram which shows the relationships among the duration of a modifying reaction operation, degree of modification, catalyst layer temperature, etc. in Application Embodiment 3.

(Explanation of notations)

- (1): Reaction tank;
- (11): Catalyst layer;
- (20): Liquid mixture of methanol & water;
- (3): Controller.

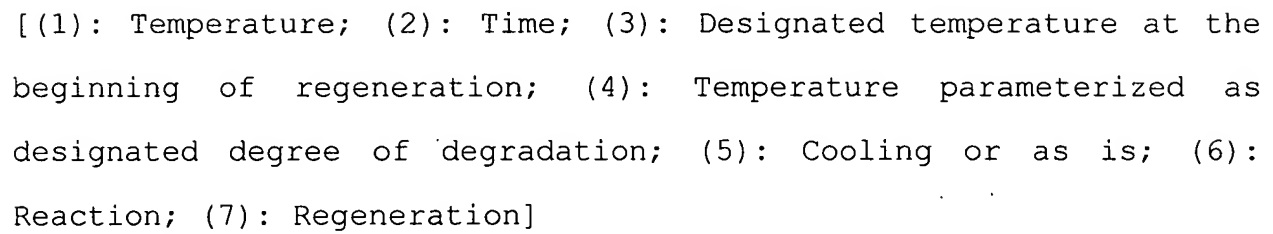
Figure 1

【図1】



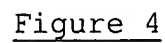
[(1): Degree of modification; (2): Temperature; (3): Time; (4): Regeneration; (5): Designated temperature; (6): Present invention; (7): Prior art]

【図2】



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【図3】



【図4】

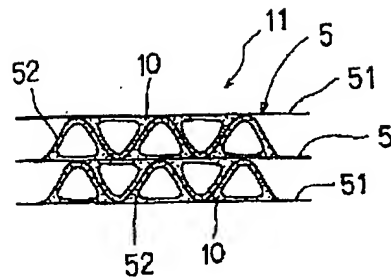
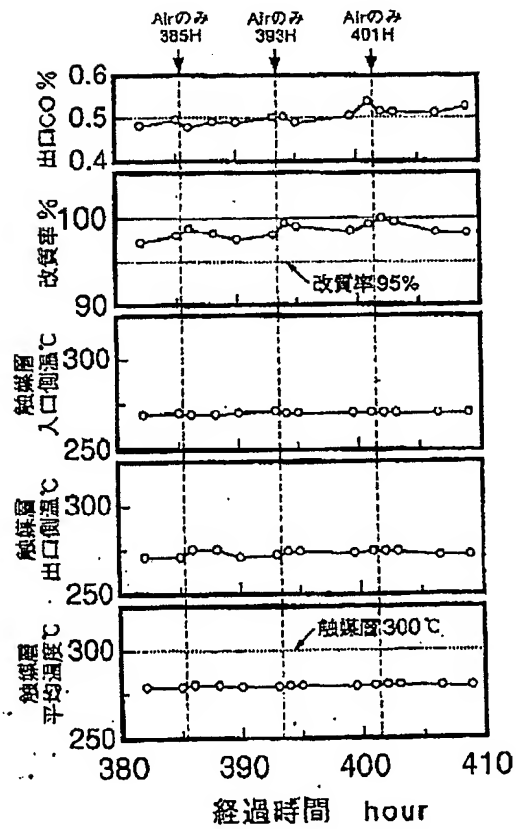


Figure 5

【図5】

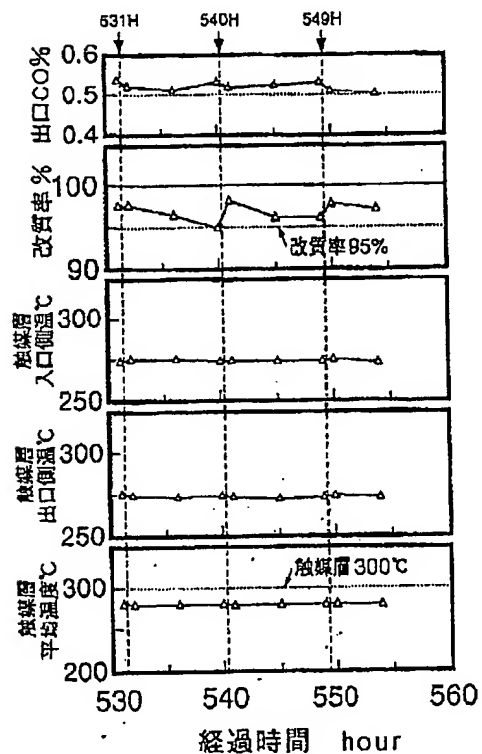


[(1): Air alone; (2): Outlet CO; (3): Degree of modification; (4): Catalyst layer inlet-side temperature; (5): Catalyst layer outlet-

side temperature; (6): Average catalyst layer temperature; (7):
Time elapsed; (8): Degree of modification; (9): Catalyst layer]

Figure 6

【図6】



[(1): Outlet CO; (2): Degree of modification; (3): Catalyst layer inlet-side temperature; (4): Catalyst layer outlet-side temperature; (5): Average catalyst layer temperature; (6): Time elapsed; (7): Degree of modification; (8): Catalyst layer]